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IN THEIR OWN WORDS

Laboratory Fellow and chemist

JAQUELINE L. KIPLINGER

explains how to maintain
a delicate balance between
serendipity and perseverance
on the path to discovery.

DOES ANYONE REALLY SET OUT TO BE A CHEMIST? I know I didn't. I went to college loosely intending to be a medical doctor. But plans have a way of shifting, bit by bit—an inspirational speaker here, a well-timed opportunity there—and as a result, my research career largely snuck up on me. I'm glad it did, and I'm glad I didn't fight it.

The first such shift in my career trajectory happened after the space shuttle *Challenger* burst into flames in a horrific midair explosion. One of my professors did a classroom demonstration illuminating the immense energy that can be released in an uncontrolled detonation, and I was captivated. Talk about making the best of a tragic situation! Just like that, a research career started to feel like a real option—and in chemistry of all things.

The same theme of chance timing, and perhaps a healthy dose of capitalizing on challenges revealed in current news and international events, seems to have guided parts of my research too. Every time I tried to solve some chemistry conundrum, whether I was ultimately successful or not, I ended up solving something else along the way, something people needed right then. Case in point: in graduate school, I set to work on Teflon™, essentially finding ways to break it down or bond to it—ways to stick to something expressly designed to be nonstick. But a Teflon molecule is a string of carbon fluorides (CF₂), and around the same time, people were really interested in the related fluorocarbons (CF₄) that contributed to the earth's ozone hole. My effort to defeat Teflon—which I considered fascinating and valuable in its own right—had positioned me to spend the next few years at the forefront of the successful international effort to assess and repair a hole in the earth's atmosphere.

I came out of that experience feeling like a serious scientist, a real expert. That feeling lasted until I got to Los Alamos as a Frederick Reines Distinguished Postdoctoral Fellow, where I quickly found out just how much I didn't know.

Can U=C it?

Since coming to Los Alamos, I spend most of my time mountain biking, gardening, hiking, and hanging out with my family, cats, and friends—and, of course, trying to make

HAVING AN OVERARCHING QUEST GUIDES NEW DISCOVERIES ON ITS PERIPHERY.

uranium atoms double-bond to carbon: U=C. For nearly two decades, I have been consistently pursuing that. (By “that,” I mean the uranium-carbon double bond. If I had spent as much time mountain biking as I spent on that double bond, then it would be embarrassing how often I still fall down.) Before I came here, I didn't know there was anything I could devote 20 years to, off and on, without solving it many times over. But actinide chemistry—uranium being an actinide element—is really hard, and achieving the synthesis of a U=C bond has enormous potential scientific and programmatic impact.

It's such a specific, simple-sounding thing to make U=C. But it just wouldn't happen, not for anyone, for a really long time. Only in the past year did my team make it happen. Sort of. Technically, we “trapped” it, which means we demonstrated a chemical reaction that would only occur if U=C had emerged along the way. We still haven't actually seen U=C itself. But at least now we know it's not completely impossible to make.

Trapping U=C has been tremendously gratifying for me. But like most scientific discoveries, it leads to more questions, more analysis, and more experiments. To be sure, my work on this is far from complete. But every once in a while, something pivotal happens, and that's how I see trapping this double bond.

For an element of such strategic importance as uranium, for both national defense and energy security, exploring all of its chemistry is obviously imperative. Here at Los Alamos, certain key aspects of our mission clearly depend on finding out everything you can do with it. From nuclear fuel to nuclear power to nuclear weapons to nuclear waste, uranium is key. People tend to focus on its nuclear properties, which stem from its nuclear physics, rather than its chemical properties, which stem from its electronic structure. But to extract it, refine it, repurpose it, store it, and really do anything at all with it, you need to understand the chemistry. And of course, the carbon I'm trying to attach it to—well, carbon is everywhere, and it's important to just about everything.

Yet I think the quest is even bigger than all that. The simple fact that this double bond is so incredibly, unexpectedly hard to make implies that something deeper is going on here—some new aspect of an atom's electronic structure that no one in the world knows about yet. And now that we've trapped it, we're much closer to understanding it.



Mother of invention

To the uninitiated (and, I suppose, to plenty of professional chemists), it may sound absurd to spend two decades pursuing this one troublesome double bond—which, by the way, other scientists had been pursuing for at least another decade before I ever got involved. And had that been my sole focus the whole time, it might have been a bit monomaniacal. But as with Teflon and the ozone hole, my uranium research produced a number of practical but unanticipated spinoff discoveries along the way.

Uranium is unique in a lot of important, useful ways. It can catalyze reactions that no other element can. It can be used to create superconductors and other specialty materials. It can be used to disintegrate petroleum contaminants. It can, of course, be configured into nuclear fuels. You study these things in the laboratory, making progress until nitty-gritty chemistry gives way to real-world materials science, and real-world materials science produces tangible technology.

But that initial laboratory work requires some starting material—some uranium compound that can be obtained,

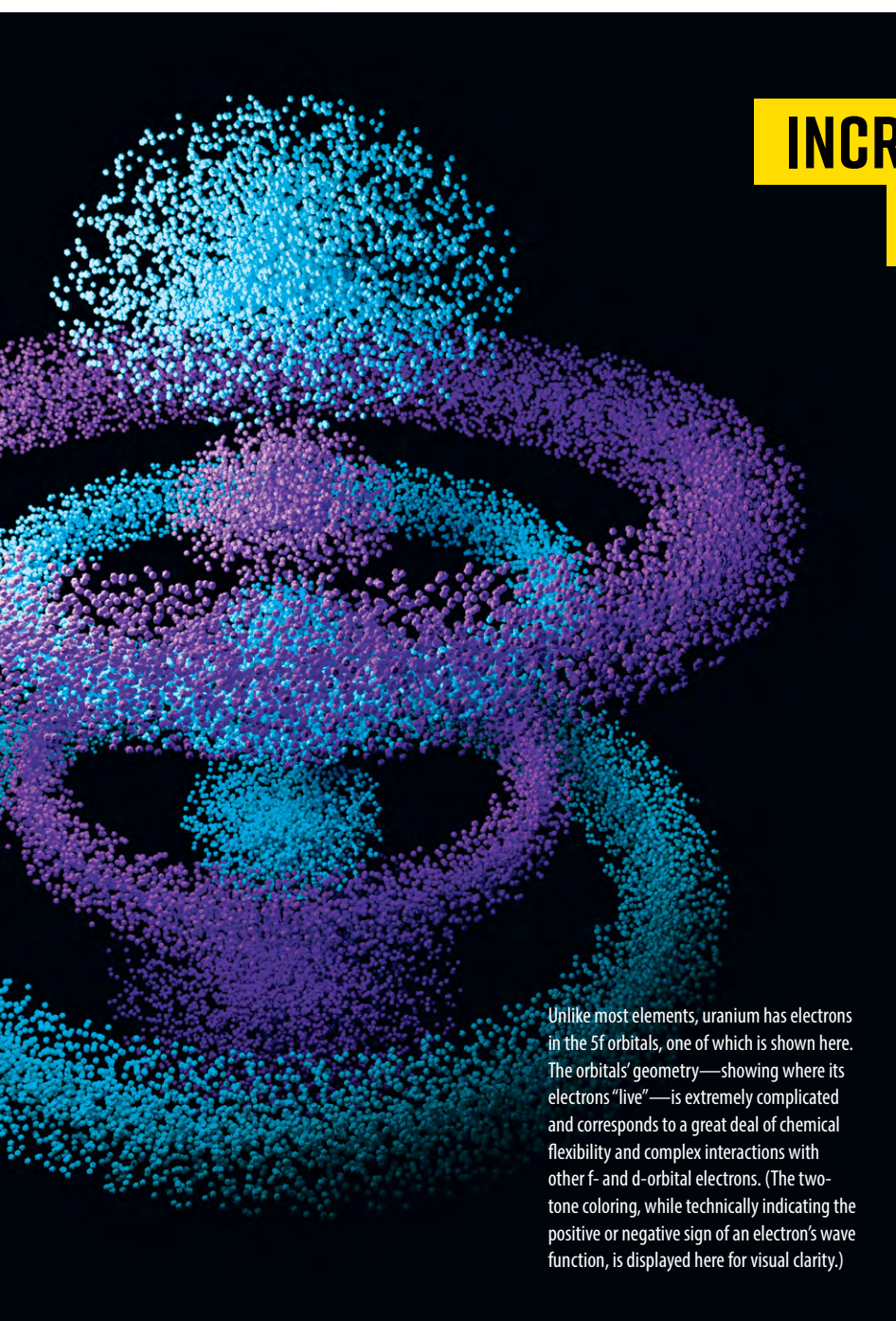
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manipulated, and experimented upon in safe, reliable, and flexible ways. And suitable uranium compounds are not so easy to come by. Before I came to Los Alamos, the processes people employed to make uranium starting materials were cumbersome, dangerous, irreproducible, and astonishingly inefficient. Some produced toxic waste. Not surprisingly, over time, various safety and security protocols have been established that limit what you're allowed to do, and these restrictions motivated my research efforts.

The point is, practical starting materials containing uranium (and ones containing thorium, neptunium, plutonium, and other actinide elements) are sorely needed. My quest for the elusive uranium-carbon double bond took me in several different directions, and one of them led me to develop new safe, inexpensive, and environmentally friendly uranium starting materials, uranium iodides, in two particularly useful oxidation states [see *"Uranium Made Easy"* in the August 2011 issue of 1663].



Unlike most elements, uranium has electrons in the 5f orbitals, one of which is shown here. The orbitals' geometry—showing where its electrons “live”—is extremely complicated and corresponds to a great deal of chemical flexibility and complex interactions with other f- and d-orbital electrons. (The two-tone coloring, while technically indicating the positive or negative sign of an electron's wave function, is displayed here for visual clarity.)



There's also important experimentation to be done on existing uranium compounds. Uranium nitride, for instance, has been proposed as a valuable nuclear fuel, and it has been produced in a practical, scalable way. My carbon quest had me working with nitrogen though, and I learned that uranium nitride is considerably more reactive with hydrogen than anticipated. Hydrogen is downright ubiquitous (in water, in plastics, in organics, etc.), which means that uranium nitride will only be a useful nuclear fuel if people can establish adequate isolation protocols that don't interfere with its use as a fuel.

Such practical applications and discoveries are a joy to find. But so are the impractical ones. Pure chemistry is a lot more captivating than early-college-me could possibly have known.

At the bottom of the periodic table

We do a really impressive job teaching chemistry in high school and college. We have the story down cold. As you work your way down the periodic table of elements, you're increasing the number of electrons on the atom. The electrons populate specific regions, called orbitals, according to a well-defined set of rules. Orbitals roughly indicate the zones that the electrons live in, and different ones have different shapes that get progressively more complicated. The s-orbitals are spherical; p's are vaguely shaped like a figure eight; d's are a mix of lobes and rings; and f's are, well, a more complicated mix of lobes and rings. Orbitals also have energy levels associated with them, and you start populating them with the lowest energies: electrons go in the 1s first: the lowest-energy s-orbital. Then the 2s. Then 2p. Then 3s, 3p, 4s, 3d, 4p, and upward, in a prescribed sequence. That's the recipe. That's the basis for the chemical



behavior of elements as we teach it. Electrons in *this* orbital are more likely to bond in *that* way.

What we don't always teach is that these orbitals and energy levels were derived for hydrogen—which has just one electron. That electron can be excited into any of these higher-energy orbitals (although it is normally in the 1s ground state). An atom with many electrons is tremendously

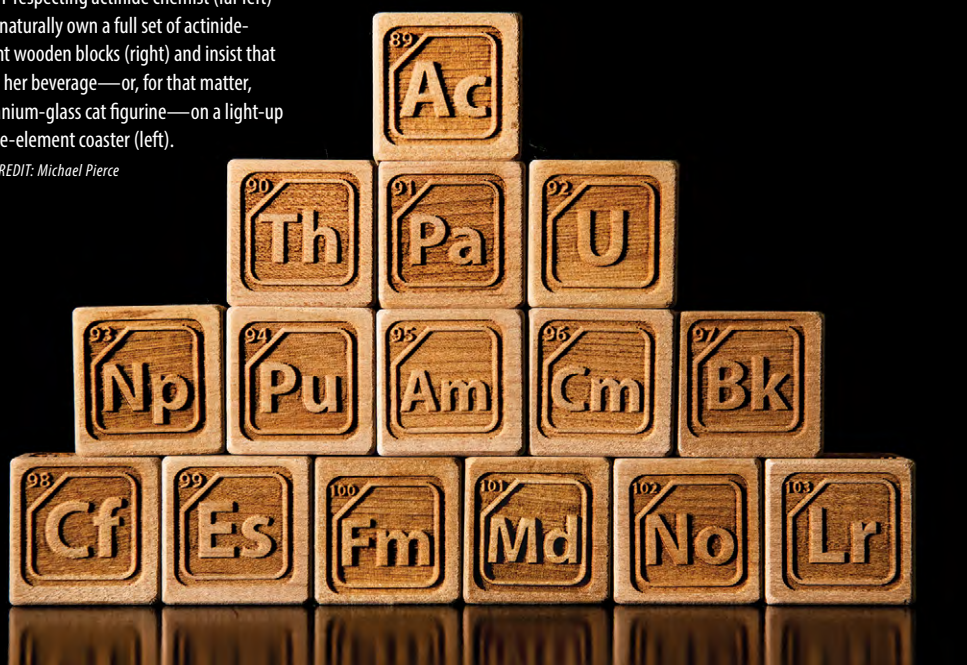
**WE KNOW
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complicated because the electrons don't just interact with the atomic nucleus, like hydrogen's lone electron does, but also with all the other electrons. We develop approximations to minimize all that complexity—approximations like “elements in the same column of the periodic table tend to act the same” or “one electron interacts with the others not individually but as though they occupy a single coherent smear that does nothing but obscure the nucleus.”

None of this is perfectly true, and when you get up to a 5f element like uranium, with 92 electrons, all bets are off. Interactions within and between atoms with occupied 5f orbitals constitute a game-changer—both introducing

Any self-respecting actinide chemist (far left) would naturally own a full set of actinide-element wooden blocks (right) and insist that she set her beverage—or, for that matter, her uranium-glass cat figurine—on a light-up actinide-element coaster (left).

PHOTO CREDIT: Michael Pierce



new behaviors and interfering with old ones—whereas, for most elements (except the actinides), the 5f orbitals generally don't get involved at all. We know s-, p-, and d-orbitals very well. We know comparatively little about f-orbital electrons, and especially the 5f actinide elements, which live at the bottom of the periodic table. It's both exciting and humbling to study them, and that's why I've chosen to make Los Alamos my professional home.

My white whale

So, what about that uranium-carbon double bond? I've been chasing it for a long time. If it can be coaxed into existence—and having recently trapped it, I think it can—it'll be a major stepping stone to producing an advanced nuclear reactor fuel called uranium carbide. It will also provide important new information to help with nuclear waste and nuclear separations technologies. And I have no doubt that making the double bond will teach us something profound about the electronic structure of actinide atoms, their materials science, and their chemical properties. After all, uranium can make this double bond with carbon's periodic table neighbors—nitrogen, oxygen, sulfur, and phosphorous, for example—but with carbon, which bonds to just about everything else in the world, it resists with all of its might. Something significant is clearly going on here.

Though it might seem like a self-imposed lifetime of professional frustration for me to keep fighting against nature, trying to make it do what it clearly doesn't want to do, I see the situation differently. This quest will ultimately pay off. Indirectly, it has already repeatedly paid off with a number of spinoff technologies—for example, with newer and better ways to produce starting materials for experimentation.

Having an overarching quest to guide my exploration has kept me focused, forcing me to make progress on the main goal while, at the same time, inspiring a number of valuable discoveries on its periphery.

My most recent spinoff rabbit hole, for example, had me examining a set of fascinating chemical constructs called aromatic actinide metallacycles. We take an aromatic, or ring-shaped, organic molecule, such as thiophene (a pentagon-shaped molecule with a sulfur atom at one vertex and carbon atoms at the other four vertices), and try to shove a uranium atom in there in place of the sulfur atom, where it has no business being—not by any natural

process we know of, anyway. The result? Its 5f electrons engage in new ways and produce unusual chemical and electronic properties. We see how they'll participate in bonding and how they won't. We see them forming chemical complexes that transition metals (like iron or gold, with accessible d-orbital electrons) and even lanthanides (like neodymium or europium, with accessible 4f electrons) just can't, thereby teaching us about some of the more fundamental aspects of chemical bonding. And as a result, we see things no one has seen before.

We're so close now to isolating the U=C double bond. And once we do, we'll be able to study its chemical and physical properties using a combination of experiment and theory. We will also be able to do the major traditional analyses on it, such as electrochemistry, spectroscopy, and crystallography. We will learn the secrets of the U=C bond and use them to do old things better and do new things altogether.

How could anyone *not* be drawn to chemistry? **LDRD**

— Jaqueline L. Kiplinger

More actinide chemistry at Los Alamos

<http://www.lanl.gov/discover/publications/1663/archive.php>

- **Aging of plutonium**
"In Their Own Words" | December 2016
- **Electron correlations**
"A Community of Electrons" | October 2015
- **New kind of covalent bond**
"Bond, Phi Bond" | January 2015
- **Uranium iodide starting materials**
"Uranium Made Easy" | August 2011